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VISIBLE LIGHT-DRIVEN GENERATION OF CHLORINE AND BROMINE, PHOTOO-- TC(U)
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electricity or contribute to the energy needed to produce X_2 . The band gaps of MoS_2 and $MoSe_2$ are about 1.1 eV and light of energy greater than or equal to this value can be used. Monochromatic, 632.8 nm, efficiencies for conversion of light to electricity, where the photoanode process is $2X^- \rightarrow X_2$ and the cathode process is $X_2 \rightarrow 2X^-$, are up to ~7% for $X = Br$ at 160 mW/cm² input optical power and up to ~3% for $X = Cl$ at 160 mW/cm² input optical power.

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TECHNICAL REPORT NO. ¹⁴ 22 ^{TR-}

⁹ VISIBLE LIGHT-DRIVEN GENERATION OF CHLORINE AND BROMINE.
 PHOTOOXIDATION OF CHLORIDE AND BROMIDE IN AQUEOUS SOLUTION AT
 ILLUMINATED N-TYPE SEMICONDUCTING MOLYBDENUM DISILENIDE AND
 MOLYBDENUM DISULFIDE ELECTRODES.

by

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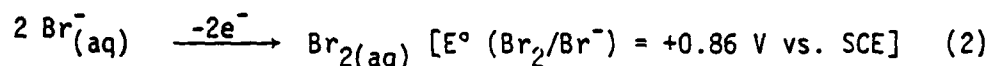
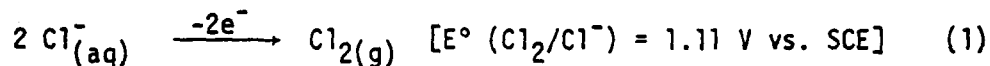
Visible Light-Driven Generation of Chlorine and Bromine. Photooxidation of Chloride and Bromide in Aqueous Solution at Illuminated N-Type Semiconducting Molybdenum Diselenide and Molybdenum Disulfide Electrodes

Abstract: N-type semiconducting, single-crystal MoS_2 and MoSe_2 are demonstrated to serve as durable photoanodes for the photogeneration of Br_2 or Cl_2 from aqueous 12 M LiBr or 15 M LiCl , respectively. The current efficiency for the generation of X_2 is measured to be >90% and many more moles of X_2 can be generated than the number of moles of MoSe_2 or MoS_2 used. Previous studies at low Cl^- or Br^- activity show only photocorrosion of the photoanode. In the 12 M LiBr or 15 M LiCl , light can be used to effect X_2 generation at a potential ~ 0.5 V more negative than $E^\circ(\text{X}_2/\text{X}^-)$ showing that the light can be used to generate electricity or contribute to the energy needed to produce X_2 . The band gaps of MoS_2 and MoSe_2 are about 1.1 eV and light of energy greater than or equal to this value can be used. Monochromatic, 632.8 nm, efficiencies for conversion of light to electricity, where the photoanode process is $2\text{X}^- \rightarrow \text{X}_2$ and the cathode process is $\text{X}_2 \rightarrow 2\text{X}^-$, are up to $\sim 7\%$ for $\text{X} = \text{Br}$ at 160 mW/cm^2 input optical power and up to $\sim 3\%$ for $\text{X} = \text{Cl}$ at 160 mW/cm^2 input optical power.

Visible Light-Driven Generation of Chlorine and Bromine. Photooxidation of Chloride and Bromide in Aqueous Solution at Illuminated N-Type Semiconducting Molybdenum Diselenide and Molybdenum Disulfide Electrodes

Sir:

We wish to report the sustained, visible light-driven oxidation of Br^- and Cl^- according to equations (1) and (2) in aqueous solutions using



n-type semiconducting MoY_2 ($Y = \text{S}, \text{Se}$) photoanode-based cells. Based on results from previous studies, the oxidizing power of the photogenerated holes at the $\text{MoY}_2/\text{liquid}$ interface is great enough (more positive than $E^\circ(\text{Cl}_2/\text{Cl}^-)$) to effect Cl_2 or Br_2 generation in aqueous solution.¹⁻³

However, in aqueous solutions photoanodic corrosion of the electrodes is the dominant process in the presence of Br^- or Cl^- ,¹⁻³ while photooxidation of I^- to I_3^- has been shown to be quite efficient at MoY_2 photoanodes in aqueous media.^{3,4} This investigation of the oxidation of aqueous Cl^- and Br^- was prompted by the findings in this laboratory that Cl^- , Br^- , or I^- could be photooxidized in non-aqueous (CH_3CN) solution without deterioration of the MoY_2 photoanode.⁵⁻⁷ We thus sought conditions where the oxidation of Cl^- or Br^- could be achieved in aqueous solutions, starting with the notion that the solvent (H_2O) could play both the role of (i) kinetic competitor with X^- for the photogenerated oxidizing equivalents and (ii) partially determining the energetics for the photocorrosion process.⁸⁻¹⁰

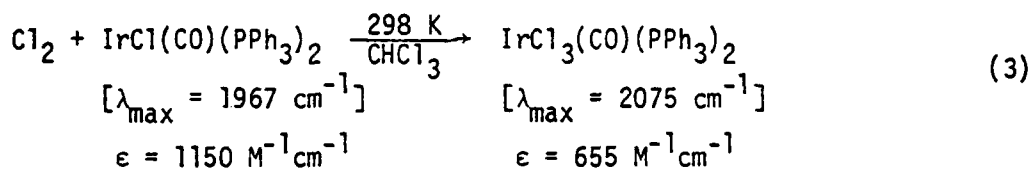
Our strategy for oxidation of Cl^- or Br^- in aqueous solution has been to employ super high concentrations of these ions by using aqueous electrolyte solutions of LiCl (15 M) or LiBr (12 M). The rationale is two-fold: (i) the effective activity of X^- can be much higher than the concentration (the Cl^- activity of 15 M LiCl is ~480 M and the Br^- activity

of 12 M LiBr is $\sim 560 \text{ M}^{11}$ to provide the kinetic advantage for productive photooxidation of X^- and (ii) the activity of H_2O can be reduced significantly by the high ionic strength¹¹ to reduce the efficiency for photocorrosion.

Visible light irradiation of the single-crystal, n-type MoY_2 anode of an electrochemical cell employing aqueous 15 M LiCl or 12 M LiBr ($pH \approx 6$) results in the anodic processes represented by equations (1) or (2), respectively.¹² Light of higher energy than the band gap, $\sim 1.1 \text{ eV}$, is effective.^{13,14} Quantitative measurements have been made using 514.5 or 632.8 nm light from an Ar ion or He-Ne laser, respectively. The cathode process is either the reduction of X_2 to $2X^-$ and/or reduction of H_2O to form H_2 depending on the amount of X_2 present.

Two facts are significant. First, the photoanodes are durable when X_2 is being generated. Second, photooxidation occurs at MoY_2 potentials up to $\sim 0.5 \text{ V}$ more negative than $E^\circ(X_2/X^-)$ showing that light can contribute up to $\sim 0.5 \text{ V}$ toward the energy needed to produce X_2 . Steady-state photocurrent-voltage curves for MY_2 photoanodes in X_2/LiX aqueous solutions are given in Figure 1. Under these conditions the dark Pt cathode process is X_2 to $2X^-$ reduction and there is no net chemical change in the cell. Data from such curves are summarized in Table I. When the MoY_2 potential is more negative than the electrochemical potential of the solution, light is converted to electricity when there is photocurrent. Efficiencies¹⁵ for the conversion of 632.8 nm light to electricity are given in Table I. The approximately 7% efficiencies for $X = Br$ are among the highest ever reported from this laboratory⁵⁻⁷ under any conditions for the MY_2 photoanodes.¹⁶ The large difference in efficiency for Cl^- and Br^- photooxidation at MoS_2 may reflect a strong interaction with the Br^- . The efficiencies show no significant dependence on input light intensity over the range used. It is noteworthy that the light intensity from the AM1 solar spectrum is only $\sim 100 \text{ mW/cm}^2$ and that the Cl_2/Cl^- and Br_2/Br^- couples are more transparent than the I_3^-/I^- couple that has previously been used in durable photoelectrochemical cells for conversion of visible light to electricity.^{4,6,7,16c,17-19}

The durability of the photoanodes is first suggested by noting that there is no obvious surface corrosion after photoelectrolytic oxidation of X^- , with or without added X_2 . When the LiX concentration is only 0.1 M the rapid surface photocorrosion is obvious on the timescale of doing experiments such as those represented in Figure 1 and Table I. Current efficiency for Cl_2 generation from 15 M $LiCl$ was measured for the MoY_2 photoanodes by collecting the Cl_2 gas (up to 15 ml) above the photoanode using an inverted graduated pipette. The Cl_2 was found to be the gaseous product by smell, color, and reaction with $CHCl_3$ solutions of $IrCl(CO)(PPh_3)_2$ as compared with an authentic sample of Cl_2 gas. The reaction of Cl_2 with $IrCl(CO)(PPh_3)_2$ proceeds according to equation (3) and can be used to quantitate Cl_2 with



molecular specificity using the infrared spectrum in the CO stretching region.²⁰ For both MoS_2 and $MoSe_2$ we find that the photocurrent efficiency is >90% without correcting for Cl_2 that is lost by dissolving in the electrolyte solution. The current density for which these current efficiencies were determined were ~10 mA/cm^2 for MoS_2 and ~45 mA/cm^2 for $MoSe_2$. These photocurrent densities were sustained for periods exceeding 50 h without obvious damage to the photoanode. In the ~45 mA/cm^2 $MoSe_2$ case, greater than 150 moles of Cl_2 were generated per mole of $MoSe_2$ without deterioration of the photoanode. Longer term tests of durability are now in progress. Experiments similar to those for Cl^- oxidation have been performed for Br^- oxidation. However, Br_2 remains in solution and current efficiency was determined spectrophotometrically as compared to authentic Br_2 in 12 M $LiBr$. The initial current efficiency for n-type MoS_2 (10 mA/cm^2) was >95% and for n-type $MoSe_2$ (70 mA/cm^2) was >90%. Again, photocurrent can be sustained and many turnovers based on the original number of moles of crystal can be

obtained. It is particularly noteworthy that we find durability at electrode potentials significantly positive of the onset of photoanodic decomposition in 0.1 M - 1.0 M supporting electrolyte (e.g. KCl, LiCl, LiBr, NaClO₄).

The durability of MoS₂ and MoSe₂ photoanode in aqueous 15 M LiCl or 12 M LiBr is the main finding. Generation of Cl₂ is the energetically most difficult oxidation process ever sustained in aqueous solution at a non-oxide photoanode. The durability is likely due to the super high X⁻ activity and the lower activity of H₂O that participates in the photocorrosion. Support for this conclusion comes from the fact that the onset for photoanodic corrosion moves more positive as the concentration of an "innocent" electrolyte LiNO₃ is increased; for example, at 0.1 M LiNO₃ the photoanodic current onset is at ~+0.2 V vs. SCE for MoS₂ while it is at ~+0.5 V vs. SCE at 10 M LiNO₃. In 10 M LiNO₃ the photocurrent efficiency at +0.7 V vs. SCE for 0.1 M Br⁻ oxidation (~30%) at illuminated MoS₂ is significantly higher than for 0.1 M LiBr alone (~0% efficiency).²¹ These data show an important role for both Li⁺ concentration and high X⁻ concentration. Further details will be reported in the full paper.²²

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12. Electrodes were prepared using materials and procedures previously described.⁵⁻⁷ LiCl and LiBr solutions were prepared by adding distilled H₂O to the solid to achieve a concentration of 15 M LiCl and 12 M LiBr. Small amounts of insoluble materials were filtered to achieve optical clarity. Solutions for steady-state photocurrent-voltage curves were prepared by adding Cl₂ or Br₂ to the LiCl or LiBr, respectively, and were stoppered to prevent escape of the X₂ from the electrochemical cell. All data are for 298 K. Samples of photogenerated gas (Cl₂) or authentic Cl₂ were added to a 9 mM IrCl(CO)(PPh₃)₂ (from Pressure Chemical Co.) CHCl₃ solution under Ar via a gas-tight Hamilton syringe with Teflon fittings. Infrared spectra of IrCl(CO)(PPh₃)₂ and IrCl₃(CO)(PPh₃)₂ were obtained using a Perkin Elmer Model 180. Br₂ was monitored spectrophotometrically using a Cary 17 uv-vis-nir spectrophotometer.
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15. When no X_2 is present the evolution of H_2 occurs at the dark Pt cathode. Thus, the net chemistry is: $X^- + H_2O \rightarrow \frac{1}{2}X_2 + \frac{1}{2}H_2 + OH^-$; when no X_2 is present at the cathode. Since the cathodic evolution of H_2 is a pH dependent process, efficiencies are generally best given with reference to the half-cell reaction driven at the photoelectrode.
16. Efficiencies for photoelectrochemical cells employing layered semiconductors such as MoS_2 , $MoSe_2$, WSe_2 have been shown to depend on the electrode materials: (a) Ahmed, S.M.; Gerischer, H. Electrochim. Acta, 1979, 24, 705; (b) Kautek, W.; Gerischer, H.; Tributsch, H. Ber. Bunsenges. Phys. Chem., 1979, 83, 1000; (c) Lewerenz, H.J.; Heller, A.; DiSalvo, F.J. J. Am. Chem. Soc., 1980, 102, 1877.
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21. The current efficiency for photooxidation of 0.1 M Br^- in aqueous 10 M $LiNO_3$ is much higher at more negative potentials, since the efficiency of the photocorrosion declines at the more negative potentials. The durability and current efficiency of MoS_2 and $MoSe_2$ in 12 M $LiBr$ and 15 M $LiCl$ were determined at +0.7 - 0.8 V and +1.1 - 1.2 V vs. SCE, respectively.
22. We note related work showing that $MoSe_2$ is a durable photoanode in aqueous solutions containing high concentrations of HBr : Ang, P.G.P.; Sammells, A.F., Third International Conference on Photochemical Conversion and Storage of Solar Energy, Book of Abstracts, Solar Energy Research Institute, Golden, Colorado 80401, p. 473.

Table I. Output Characteristics for n-Type MoS_2 and MoSe_2 -Based Photoelectrochemical Cells,

Electrolyte	Photoanode	Input ^a mW/cm^2	ϕ_e^b	Max Power Output, mW/cm^2	Max V (V at η_{max}^c)	η_{max}^d	Fill Factor ^e
H_2O , 15 M LiCl 0.04 M Cl_2 $E_{\text{redox}} =$ 1.03V vs. SCE	MoSe_2	28	0.51	0.87	400 (190)	3.1	0.30
		85 ^f	0.35	2.4	480 (230)	2.9	0.34
		160	0.50	5.6	530 (230)	3.5	0.26
H_2O , 12 M LiBr 0.05 M Br_2 $E_{\text{redox}} =$ 0.69V vs. SCE	MoS_2	27	0.29	0.2	400 (110)	0.7	0.29
		98 ^f	0.34	1.0	450 (110)	1.1	0.34
		270	0.28	4.2	520 (170)	1.6	0.28
H_2O , 12 M LiBr 0.05 M Br_2 $E_{\text{redox}} =$ 0.69V vs. SCE	MoSe_2	7.3	0.60	0.51	410 (280)	7.0	0.60
		29	0.61	2.1	480 (300)	7.5	0.61
		88 ^f	0.61	6.9	530 (320)	7.9	0.61
		160	0.62	12	570 (320)	7.8	0.62
H_2O , 12 M LiBr 0.05 M Br_2 $E_{\text{redox}} =$ 0.69V vs. SCE	MoS_2	7.2	0.69	0.45	460 (240)	6.2	0.69
		28	0.68	2.1	520 (300)	7.4	0.68
		87 ^f	0.69	6.1	570 (280)	7.0	0.69
		160	0.70	11	600 (280)	7.2	0.70

^a Input power is the 632.8 nm line from a Coherent Radiation He-Ne laser.

^b Quantum yield for electron flow at E_{redox} ; this corresponds to the short-circuit quantum yield taken as the number of electrons passed per incident photon.

^c Maximum voltage is the open-circuit photopotential and the number in parentheses is the output voltage at the maximum power point.

^d Efficiency for the conversion of 632.8 nm light to electricity.

^e Fill factor is a measure of the rectangularity of the current-voltage curves (Figure 1) and is defined as the $(\text{max power})/(\text{max V} \times \text{short-circuit photocurrent})$.

^f

Figure Caption

Steady-state photocurrent-voltage curves for n-type MoS_2 (left frames) and n-type MoSe_2 (right frames) photoanode-based cells. Illumination was at 632.8 nm under the conditions indicated.

